Carbon dioxide hydrates crystallisation in emulsion

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CARBON DIOXIDE HYDRATES CRYSTALLISATION IN EMULSION

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ABSTRACT

Greenhouse gases emissions, like carbon dioxide, have been identified as major sources responsible for global warming. To reduce carbon dioxide emissions, capture process can be envisaged to extract CO_2 from flue gases. In this work, the technology of CO_2 separation and capture by gas hydrates crystallization is investigated. The principal barriers in developing this process are the necessary high conditions of formation (P, T), low hydrates formation rate, and separation efficiency. A promoter additive, the cyclopentane (CP), is proposed to improve the quality of the capture both at the thermodynamic and kinetic levels. An experimental study looking at the influence of the CP content on the kinetic of gas hydrates formation is presented. CP has been studied as a dispersed phase (emulsion) or as a secondary and clearly distinguished second phase. The rate of crystallization (gas consumption rate) reveals to be very different according to the CP dispersion. The system is oriented to form pure gas hydrates in one case, or mix CP-Gas hydrates in the other case. Finally, several equilibrium points of CP-CO_2 hydrates are obtained. The results demonstrate that cyclopentane is a good additive which can remarkably decrease the gas hydrates formation pressure and enhances the formation rate.

Keywords: gas hydrates, cyclopentane, emulsion, kinetic, thermodynamic

NOMENCLATURE

d Precision [g]
$n_{CO2,i}$ Initial mol number (gas phase) [mol]
$n_{CO2,n}$ Nucleation mol number (gas phase) [mol]
$n_{CO2,f}$ Final mol number (gas phase) [mol]
P Pressure [bar]
P_{alim} Alimentation pressure [bar]
P_{eq} Equilibrium pressure [bar]
R Perfect gases constant [$J.mol^{-1}.K^{-1}$]
r_{dis} Dissolution rate [$mol.h^{-1}$]
r_{5hours} Growth rate in five hours [$mol.h^{-1}$]
r_{moy} Average growth rate [$mol.h^{-1}$]
t Time [h]
t_{ind} Induction time [h]
T Temperature [K]
T_C Setpoint Temperature [K]
T_{eq} Equilibrium Temperature [K]
T_{liq} Liquid Temperature [K]
V_G Gas volume [m^3]
V_L Liquid volume [m^3]
V_r Reactor volume [m^3]
Z Compressibility factor [-]
Δ Difference [-]

INTRODUCTION

Greenhouse gases emissions, like carbon dioxide, have been identified as major sources responsible for global warming. Carbon dioxide is essentially produced by combustion of fossil energy, like in power generation plant. One possible way to reduce these emissions is to install an industrial process that can be integrated in the existing installations to extract CO_2 from flue gases.
Several capture processes exist. We can mention absorption by MEA, membrane or physical adsorption.

As the flue gases are at low concentration in CO_2 (typically 5%-15 % in power plant) and at high flow rates (several cubic meters per second of CO_2), the capture technology needs to run at severe conditions and to minimize the cost of the process
Innovative technology capture by gas hydrates crystallization can be an alternative process. For high concentrated mixtures of CO_2 in nitrogen

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(steel making plant, at atmospheric pressure), Duc and al.[1] showed that hydrates capture can be a competitive process. CO_2 trapping from gases mixture (CO_2/N_2) can be effective in a multistage separation and is then economically possible [1].

Gas hydrates are ice-like crystalline compounds formed from a combination of water and suitable guest molecules (like CO_2, N_2), under low temperature and high pressure [2]. Pure gas hydrates can store a large quantity of gas (typically 160 volumes (STP) of methane per volume of hydrates [3]).

To reduce the high pressure necessary to form gas hydrates, a small amount of additive can be used. In literature, cyclopentane (CP) is described as an excellent promoter [4-9]. It forms structures II hydrates at a temperature near 280 K and at atmospheric pressure [4].
Among the thermodynamic promoters that can be used, such as TBAB [3], [10] (tetra-n-butyl ammonium bromide) or THF [11], [11-15] (tetra-hydrofurane), CP presents the constraint to be immiscible with water. So, the equilibrium pressure of CO_2/CP hydrates is independent of CP quantity if CP is in excess. From a kinetic point of view, CP has revealed to be a promoter (Zhang and al. [7]).

In this work, the crystallization of CO_2/CP hydrates is studied. The kinetic effect of CP on the crystallization step is evaluated and the thermodynamic behavior is investigated.
Two systems (cyclopentane dispersed in a emulsion, or cyclopentane in a clear second phase) are studied to compare their effect on the hydrates formation rate [5]. Several ratio of CP (1.625% to 15% v CP/v water) are tested. Also, the benefice of CP has been investigated in a (Pressure, Temperature) domain in which CP/CO_2 binary hydrates and CO_2 gas hydrates can occur simultaneously. Another (Pressure, Temperature) domain has been investigated in which only CP/CO_2 binary hydrates can crystallize.

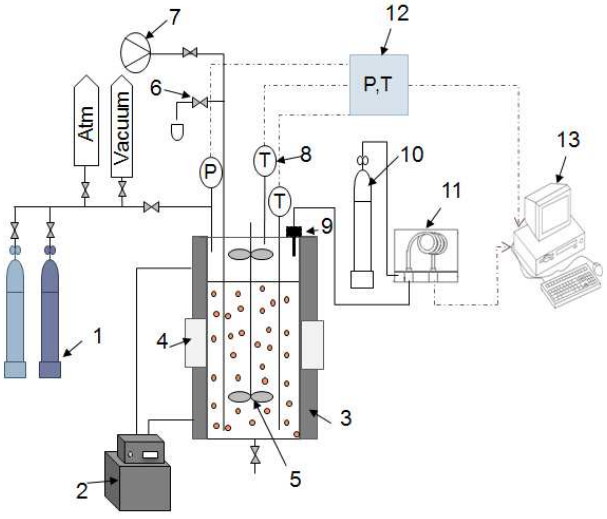
EXPERIMENTAL PROCEDURE

Experimental set up

The experimental apparatus (figure 1) allows to investigate the thermodynamic equilibrium conditions of gas hydrates (pressure and temperature) and to study the kinetic effect of promoters.
The experiments are performed in a stirred batch reactor (autoclave, 2.46 L) cooled with a double jacket. Two Rushton turbines mix both gaseous and liquid phases, so that liquid and gaseous phases are considered as homogeneous phases.
Two windows (12x2cm, polycarbonate), mounted on both sides of the reactor, allow to detect the occurrence of hydrates phase by direct visual observation.
The solution to be tested is poured in a pyrex cell, located in the autoclave, in which the pressure can be raised up to 100 bar.
Two Pt100 sensors (Prosensor instrument, precision 0.1K) give the temperatures of the liquid and the gaseous phases. The pressure is measured with a pressure transducer (range: 0–10 MPa, Keller instrument, precision of 0.1 bar). The data acquisition unit (T, P) collects the (P,T) evolution during hydrates crystallization.
The system is cooled or heated by a thermostat HUBER CC3-K6 with an accuracy of 0.1 K.
The liquid can be injected into the pressurized reactor by using a HPLC pump PU-1587 from JASCO.

The gas phase is supplied using gas cylinders and transferred to the reactor by a set of valves. The composition of the gas phase is determined in line by using a gas chromatograph, after sampling by a ROLSI instrument. This tool collects a controlled volume of gas (1-5 μm^3) which is directly injected into the loop of the gas chromatograph (VARIAN model 450 GC). This system allows to control the purity of the gas (CO_2).

This work presents a set of experimental data on CO_2-CP hydrates system.



1 gas cylinder (CO_2)
2 Cryostat
3 Reactor sell (2.46L)
4 Viewing windows (12*2 cm)
5 Stirrer
6 Liquid sampling
7 HPLC Pump
8 PT 100 Temperature sensor
9 Rolsi gas sampling
10 He alimentation
11 In line gas chromatography
12 Pressure and temperature view
13 Data acquisition (P,T)

Figure 1 Experimental set up

Preparation of cyclopentane in water emulsion

Table 1 reports the purity and suppliers of the different products used. All experiments are performed with purified water (Milli-Q plus 185).

component	Purity	Supplier
CO_2	>99.995%	Air Liquide
C_5H_{10}	>95%	Alfa Aesar
IPE 202[a]		IFP Energies nouvelles

Table 1. Purities and suppliers of components

IPE 202 is a surfactant and anti-agglomerate additive. It stabilizes the emulsion and limits the agglomeration of hydrates particles.

IPE 202 (0.45% water mass) and water are weighed by a Mettler balance (precision d=0.01g). Then, a volume of cyclopentane is added.

CP dispersed as an emulsion or CP and water in separated phases

Following the previous work of Li and Fan [5], we have investigated the influence of CP as a dispersed phase, or as a clear and separated phase from water. After pouring IPE 202, water and CP in the Pyrex cell, the emulsion is obtained by using an Ultra-turax (IKA T50) at stirring rate of 8800 tr/min. Fine CP droplets of some micrometers are obtained (figure 2).

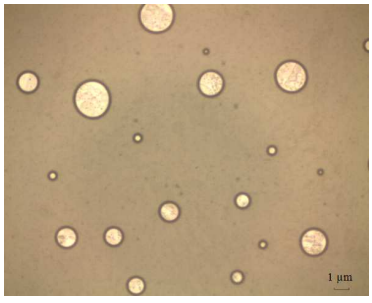


Figure 2 Microscope photograph of CP (2.50 % vol.) in emulsion.

Crystallization procedure

The Pyrex cell (containing the solution or the emulsion) is placed in the reactor and stirred at 400 rpm. The temperature of the thermostat is decreased to the crystallization temperature (T_c=274.15 K) and maintained to this value during all the crystallization process. When the liquid temperature reaches the equilibrium temperature, the stirrer is stopped and the reactor is vacuumed and then flushed with CO_2 (three to four times).

Afterwards, the reactor is charged with CO_2. The gas phase is sampled with the ROLSI© instrument and in-line analyzed by gas chromatography to check CO_2 purity. During the introduction of CO_2 in the reactor, the stirring is stopped. The gas dissolution is considered as null. Then, the stirrer is immediately switched on. The pressure decrease (figure 3) puts into evidence the dissolution of the gaseous component in liquids (water and cyclopentane).

After a few time, a sudden increase of the temperature (exothermic process) indicates the appearance of first crystals (nucleation). During the formation of the crystals, the pressure decreases due to the gas consumption to form hydrates. After a while, Pressure and Temperature reach equilibrium (end of crystallization).

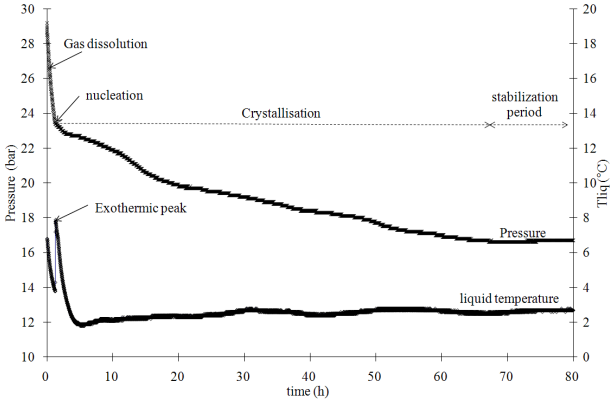


Figure 3 Crystallization step: Evolution of pressure and liquid temperature versus time. (CP in emulsion, CP = 2.50% vol)

Dissociation procedure

The gas hydrates dissociation is operated at constant volume and started by heating the reactor with steps of 1K/h. Each step of temperature is considered to be at equilibrium [8].
As the temperature increases, the pressure raises in proportion to the gas desorption. As Gas/liquid water/liquid CP/hydrates equilibrium is reached, a change in dP/dT is observed and gas hydrates dissociation starts. Pressure increases dramatically, until total gas hydrates disappearance. Then, a sudden decrease in dP/dT shows the end of dissociation.

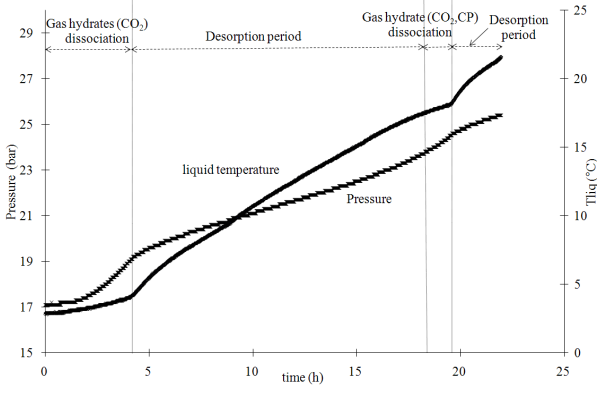


Figure 3 Dissociation step: Evolution of pressure and liquid temperature versus time (CP in emulsion, CP = 2.50% vol.)

RESULTS AND DISCUSSION

CP kinetic effect: CP as a dispersed phase

CP %v/v water	P_{alim}/ bar	P_{eq}/bar	T_{eq}/K
1.63	29.8	16.2	275.7
2.50	29.2	16.6	275.8
5.00	30.2	17.4	276.1
10.00	29.9	16.0	275.2
15.00	30.8	19.5	275.4

Table 2. Experimental data: CP in emulsion

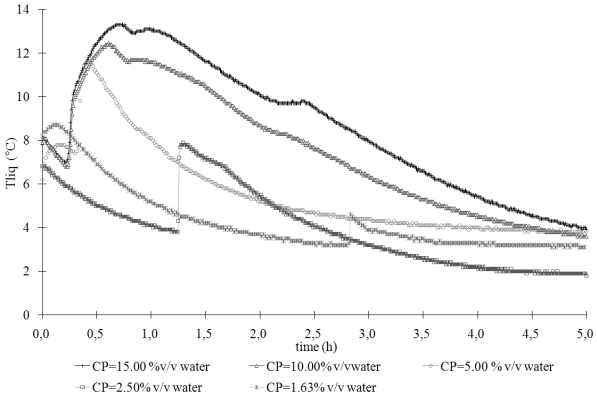


Figure 4 Liquid temperature evolutions versus time during the first five hours of the crystallization with different CP volume ratio (CP in emulsion)

CP %v/v water	t_{ind} (h)	ΔT (K)	r_{5hours} (mol/ h) $x10^{-2}$	r_{moy} (mol/ h) $x10^{-2}$
1.63	2.71	1.4	1.21	0.70
2.50	1.24	4	1.90	1.05
5.00	0.33	4.3	9.82	1.30
10.00	0.23	5.7	13.70	1.13
15.00	0.23	6.3	15.50	2.22

Table 3 Kinetic information: CP in emulsion

Figure 4 shows the exothermic peak due to the crystallization. With a low CP concentration (1.63 % vol), crystals nucleation (which usually takes a long time and is random) occurs in a few hours (see values in table 3) and seems dependent of the CP quantity.
The intensity of the temperature peak (table 3) seems proportional to the CP content. It suggests that the nucleation strength depends on the availability of the CP. It is also dependent of the

total surface of exchange between CP and water. The value of the surface increases versus CP content (CP droplet size has observed to be independent on the CP quantity).

When the nucleation occurs, the large increase of the temperature conducts the system to be out of the pure CO_2 hydrates formation area. It means that the CP/CO_2 hydrates forms and heats the solution out of the CO_2 hydrates formation area. But as temperature decreases, it re-inters in the CO_2 hydrates formation area and allows a competition between the formations of the two types of hydrates.

The intensity of the exothermic peak is directly proportional to the initial quantity of CP, so we can say that the quantity of CP/CO_2 gas hydrates is also proportional to the initial quantity of CP. The respective quantities of CO_2 gas hydrates and CP/CO_2 hydrates can be evaluated during the dissociation step. Indeed, when hydrates dissociation occurs, the (Pressure,Temperature) coordinates follow the respective equilibrium curves of CO_2 hydrates and CO_2-CP hydrates (figure 5). The respective quantities can be then calculated. . In the experiments with 10.00 % or 15.00 % vol. of CP, practically no CO_2 gas hydrates has been produced. All CO_2 has been consumed in the CP/CO_2 hydrates formation (figure 5).

It confirms the previous assumption: CP/CO_2 binary hydrates crystallization appears in the beginning of the process and after CO_2 gas hydrates crystallization can occur or not depending on the intensity of the heating. No exothermic peak for CO_2 gas hydrates is observed (the nucleation can not be located) but the coexistence of the two types of gas hydrates is confirmed by the dissociation curve.

This study is in agreement on the Li and Fan's [5] and Zhang and al.[8] studies.

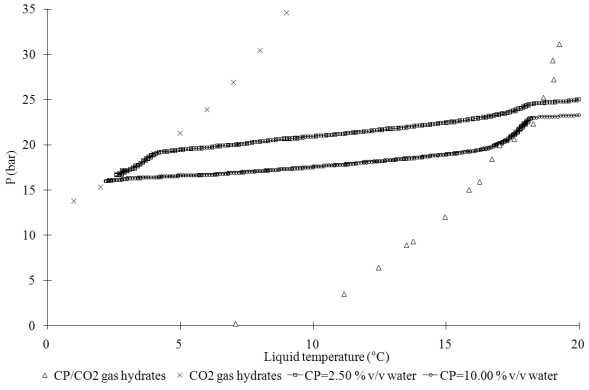


Figure 5 CP in emulsion
Evolution of pressure and liquid temperature versus time during dissociation
◊: CP-CO_2 gas hydrates [4], [8], [17].
x: simulation from GasHyDyn software

At a pressure of 23.4 bar (2.5% vol. CP), the supercooling for CO_2 hydrates is around 2 K whereas for CO_2-CP gas hydrates, supercooling is equivalent to 14.5 K (figure 6). At the beginning of the crystallization, the CO_2 consumption is fast (table 3, value for r_{5hours}) due to the CO_2-CP gas hydrates crystallization, then the CO_2 consumption slows down (table 3, r_{moy}) for the following several causes.

First at all, the emulsion becomes a concentrated slurry during the crystallization process, and CO_2 gas transfer starts to be slowed down.
Secondly, as the suspension becomes very dense, the gas hydrates tend to agglomerate at the periphery of the Pyrex cell ([7]) to form a crust which slows down the temperature transfer and generates a temperature gradient within the reactor: cooling becomes difficult at the center of the Pyrex cell where the remaining water could crystallize.
Finally, the driving force (which is initially around 2K for CO_2 gas hydrates) decreases during the crystallization process because pressure decreases. (P,T) formation conditions join the CO_2 equilibrium curve and crystallization runs slowly (due to the low driving force) (except 15% vol. CP, where only CP-CO_2 gas hydrates were produced).

Consumption rates are calculated by the equation (1) with $n_{CO2,n}$ as the initial mol number of CO_2 and $n_{CO2,5hours}$ or $n_{CO2,f}$ as the final mole number of CO_2.

$$r_{dis} = \frac{n_{CO2,i} - n_{CO2,5hours\ or\ f}}{\Delta t} \quad (1)$$

Where CO_2 mole number is calculated by:

$$n_{CO2} = \frac{PV_G}{Z(P,T)RT} \quad (2)$$

The compressibility factor Z is calculated by the Soave-Redlich and Kwong (SRK) equation of state (EOS) with parameters from Danesh [16].
The reactor gas volume is given by:

$$V_G = V_R - V_L \quad (3)$$

Consumption rate (table 3) increases with the CP volume ratio in the emulsion. The crystallization strength is dependent of the CP droplets quantity. It means that the crystallization rate is not only dependent on the gas transfer rate at the gas/liquid interface, but also on the liquid/liquid transfer rate at the emulsion interface.

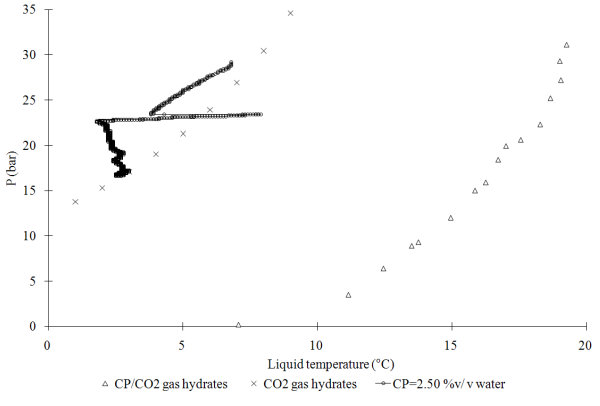


Figure 6 CP in emulsion
Evolution of pressure and liquid temperature versus time during crystallisation
◊: CP-CO_2 gas hydrates [4], [8], [17],
x: simulation from GasHyDyn software

CP kinetic effect: CP and water in separated phases

CP %v/v water	P_{alim}/ bar	P_{eq}/bar	T_{eq}/K
2.50	32.0	16.1	275.8
5.00	32.1	16.2	275.8

Table 4 Experimental data: CP/ water in different phases

CP %v/v water	t_{ind} (h)	ΔT (K)	r_{5hours} (mol/ h) x10^{-2}	r_{moy} (mol/ h) x10^{-2}
2.50	1.67	1.3	14.3	3.42
5.00	1.98	0.3	8.08	3.00

Table 5 Kinetic information: CP/ water in different phases

When CP and water are in two different phases, CP has a different kinetic effect from the CP in emulsion system [5].
Firstly, the CO_2 dissolution rate reveals to be independent on the CP volume. CP has a lower density than water. Due to the configuration of the system, CO_2 dissolves in CP at the CO_2/CP interface and then CO_2 transfers from CP to water at the CP/water interface. The rate of dissolution becomes dependent on the interfacial resistances which are independent to the volume but only proportional to the surface.
The difference in time induction can not be explained clearly, not only because the induction time is often a stochastic phenomena, but also because of the process initial conditions. In the case of 5.00% vol CP, the CO_2 dissolution is started at a higher temperature. The achievement of CO_2 supersaturation takes then longer time.

Li and Fan [5] have performed CO_2/N_2 crystallization with CP in emulsion and CP in a separated phase. They have only crystallized CO_2/N_2/CP gas hydrates and we cannot completely compare their experiments to ours. Contrary to their study, at same or equivalent CP percentage, crystallization in the separated phase system seems faster (r_{5hours}, r_{moy}) than in the emulsion. Theses values can be explained by the crystallization behavior.
If CP-CO_2 gas hydrates can be formed, one mole of CO_2 can produce a higher quantity of solid in comparison of pure CO_2 gas hydrates. Indeed, a part of the cavities are occupied by CP and not by CO_2.
During crystallization from CP in emulsion, a double effect is observed: because CP is well dispersed, the crystallization rate is enhanced, and because of the crystallization rate improvement, the temperature is heated (figure 6) in a domain in which pure CO_2 gas hydrates cannot be formed. CO_2 is then only consumed to form CP- CO_2 gas

hydrates. The liquid water is quikly immobilized under the solid form. The solution becomes very viscous: mass and heat transfers fall down and gas consumption rate decreases.

During crystallization from CP in a clear and separated phase from water, the CP transfer is limited and the rate of crystallization is decreased. The exothermic peak is low (table 5) and the pure CO_2 gas hydrates can continue to form. One mole of CO_2 can not form a large volume of solid (in comparison to CP-CO_2 hydrates): the suspension remains well dispersed and gas transfer can continue to be efficient. In this case, the gas consumption rate maintains high to form essentially pure CO_2 gas hydrate: contrary to the previous case (CP in emulsion), the gas consumption rate decreases rapidly because it forms a huge quantity of CP-CO_2 hydrates which affects negatively the gas to liquid transfer rate.

CP thermodynamic effect

Fan and al. [4] are reported that the quadruple point (CP-CO_2 gas hydrates) is at 280.22 K and 19.8 kPa. Mohammadi and al. [17] are shown that cyclopentane is the strongest hydrates promoter with neopentane in the second place.

In this paragraph, the thermodynamic promotion effect of CP is investigated. The crystallization is only performed in the CP-CO_2 gas hydrates area (Table 6 and figure 7).

The crystallization occurrence is checked by the dissociation step. Some CP-CO_2 equilibrium points are obtained and allow to complete the literature data.

CP / % v/v water	**P_{alim}/ bar**	**P_{eq}/bar**	**T_{eq}/K**
5.00	10.4	3.6	275.7
20	8.4	0.5	277.8

Table 6. Experimental data: CP in water emulsion

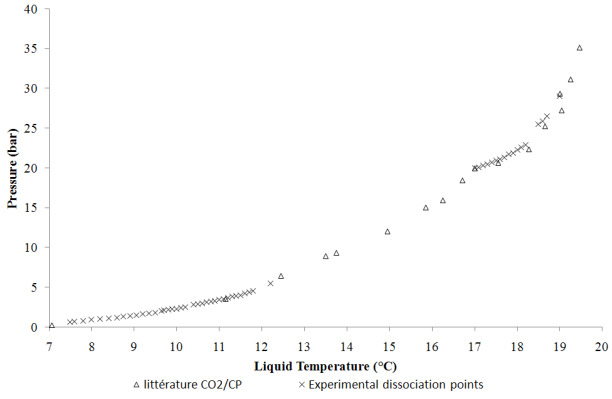


Figure 7 Experimental dissociation conditions for hydrates of carbon dioxide and cyclopentane. Δ: Literature data [4], [8], [17], x: our work

CONCLUSIONS

In this work, CP has been used to enhance the crystallization kinetic using two approaches.
When CP is dispersed into an emulsion, time induction is shorter (0.23 to 2.71 hours versus CP volume ratio) and exothermic peak (crystallization power) is higher (1.4 to 6.3K versus CP volume ratio). But gas consumption rate is affected by the strength of the process and becomes rapidly low (formation of CP-CO_2 hydrates, high concentrated slurry).

In the second case, CP is at the water surface (in different phases): time induction is around two hours, and pure CO_2 hydrates are suspected to be formed. The solid fraction is lower and don't affect the mass transfer. The consumption rate can maintain high.

In the both systems, two hydrates types (CP/CO_2 hydrates and CO_2 hydrates) have been produced. The relative ratio of the hydrates depends on the CP ratio volume, but also on the quality of the CP dispersion. A well dispersed emulsion will generate essentially CP/CO_2 hydrates, whereas pure CO_2 hydrates will be generated if the CP is badly dispersed. Finally, crystallization has been practiced only in the CP/CO_2 hydrates area. Gas hydrates have been obtained at a pressure lower than 1 bar. Equilibrium points of CP/CO_2 binary hydrates complete the equilibrium data from litterature.

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